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In-situ XAFS measurements of amorphous Li₃PO₄-doped V₂O₅ cathode for all-solid-state thin-film Li-ion batteries

Keisuke Omosako¹, Takeshi Watanabe², Satoshi Ogawa³ & Isaku Kanno^{1⊠}

In this study, in-situ X-ray absorption fine structure (XAFS) measurements were conducted on amorphous Li_3PO_4 -doped V_2O_5 (VO-LPO) cathode in an all-solid-state thin-film lithium-ion battery to observe the behavior of Li ions during charge/discharge. The thin-film lithium-ion battery was fabricated by sputtering deposition and consisted of an amorphous multilayer structure with VO-LPO, LiPON, and Si as cathode, electrolyte, and anode, respectively. In X-ray absorption near edge structure (XANES) measurements, the energy shift of the Vanadium K-edge indicated that the valence of V changed from 4.64 to 5.11 in the cathode during charge/discharge processes. This result indicates that Li ions were removed and inserted into the amorphous VO-LPO cathode layer. The pre-edge peak intensity also increased during charging and decreased during discharging. Additionally, extended X-ray absorption fine structure (EXAFS) measurements indicated that the V-O bond distance shifted during charge/discharge process. From these measurements, we clearly observed that the coordination symmetry and structure around V in the amorphous VO-LPO cathode changed with the charge/ discharge reaction.

In recent years, all-solid-state Li-ion batteries (LIBs) have attracted considerable attention due to their potential to significantly enhance energy density and safety compared to conventional LIBs using liquid electrolytes^{1,2}. The major application of all-solid-state LIBs is, in addition to portable communication devices and various home appliances, now being actively investigated for their integration into electric vehicles, which require high-power storage. On the other hand, since all-solid-state LIBs are composed of solid materials, they can be fabricated using thin-film deposition techniques such as sputtering and evaporation used in semiconductors and electronic components. All-solid-state thin-film LIBs (TF-LIBs) composed of multilayer thin films have a small total power storage capacity due to their limited amount of active materials. However, they can be integrated into microsensors and semiconductor devices, and are strongly expected to be applied as new functional devices^{3,4}. A typical configuration of TF-LIBs is LiCoO₃, Li metal as the cathode, and anode⁵⁻⁷. A number of studies have been conducted on the prototyping and evaluation of TF-LIBs using this specific material composition. Some of these batteries have been implemented in practical applications⁸. However, materials such as crystalline LiCoO₂ require high-temperature deposition or post-annealing treatment, and furthermore, Li metal is highly reactive with the atmosphere, which strongly restricts the choice of substrate and cell structure. As a result, it is difficult to enhance the capacity and power of TF-LIBs with a combination of these materials through multilayering or to deposit TF-LIBs on organic materials.

To solve the above problems, we fabricated the TF-LIBs consisting of amorphous layers which can be prepared by room temperature deposition without intentional substrate heating or post-annealing^{9,10}. The TF-LIBs were composed of LiPON as the electrolyte, and amorphous V_2O_5 doped with Li₃PO₄ (VO-LPO) as the cathode, and Si as the anode, respectively. Vanadium oxide has been investigated as an excellent cathode material for LIBs. It is reported that crystalline V_2O_5 forms an irreversible phase when discharged to low potentials^{11,12}. Thus, the reversible capacity is limited to 292 mAh/g in crystalline V_2O_5 . On the other hand, amorphous V_2O_5 has no irreversible phase formation and can overcome the operating voltage limitation. Therefore, it has been reported to achieve reversible capacities as high as 600 mAh/g, making it an excellent cathode for TF-LIBs^{13,14}. On the other hand, Si is one of the most promising anode materials due to its high capacity. Since each Si can potentially accommodate up to 4.4 Li ions, its theoretical capacity is 4200 mAh/g^(15,16). Especially, amorphous Si thin film

¹Department of Mechanical Engineering, Kobe University, Kobe, Japan. ²Synchrotron Radiation Research Institute, SPring-8, Sayo, Japan. ³Department of Energy Engineering, Graduate School of Engineering, Nagoya University, Nagoya, Japan. ^{Sem}email: kanno@mech.kobe-u.ac.jp

deposited on Ni foil was reported to maintain 3000 mAh/g through 1000 cycles, a significant improvement in practicality has been expected¹⁷. LiPON is an ionic conductive material obtained by RF magnetron sputtering on a Li₃PO₄ target in N₂ gas. Thin LiPON films have been found to have ionic conductivity of 1.2×10^{-6} S/cm and electronic conductivity of 8.0×10^{-14} S/cm at room temperature¹⁸. We selected LiPON as a solid electrolyte because it has high electrochemical stability and can be fabricated by a room temperature process.

Although charge/discharge reactions of the amorphous TF-LIBs were observed in our previous study, the capacity was low and the detailed behavior of Li ions in the TF-LIBs was still unclear. In this study, to clarify the charge/discharge reactions in amorphous TF-LIBs, in-situ X-ray absorption fine structure (XAFS) measurements were conducted to observe the valence change of active material accompanying the desorption and insertion of Li ions and the structural change of the active material during charge/discharge reactions using X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) measurements^{19,20}.

Results XANES

XANES

The TF-LIB was composed of a VO-LPO cathode, LiPON electrolyte, and Si anode, and each layer was deposited by RF magnetron sputtering. The deposition conditions were same as our previous studies^{9,10}. The structure of the TF-LIB is shown in Fig. 1a–c. XAFS measurements were conducted using synchrotron radiation at SPring-8 (BL14B2) to observe the Li ion behavior in the VO-LPO cathode layer during the charge/discharge reaction. XAFS measurements were conducted on the Vanadium K edge (V K edge) in the VO-LPO cathode. Before the XAFS measurements of the TF-LIB, the K-edge of the reference samples, vanadium metal (V), vanadium dioxide (VO₂), and vanadium pentoxide (V₂O₅) were measured. Supplementary Table 1 shows the charge/discharge conditions, and Fig. 1d presents a time sequence of the charge/discharge reaction (0.5–5.5 V) at a constant current (CC), and the XAFS measurements were conducted at a constant voltage (CV) condition. The current during the CC mode was set at 2.0 μ A (approximately 1 C). Note that "SOC 100%" and "SOC 0%" are defined as the charging and discharging states reaching 0.5 V and 5.5 V, respectively. Furthermore, since the charge/ discharge rate is about 1 C, we also defined "SOC 50%" at 30 min after the charge/discharge starts. XAFS measurements were conducted at the SOC of 0%, 50% and 100% as shown in Fig. 1d. After XAFS measurement at the initial state, charge/discharge cycle was repeated three times.

Figure 2a-b shows the XANES spectra of V during the 3rd cycle of the charging and discharging process. Generally, the K-edge is determined from the first derivative peak of the XAFS spectrum, but a clear peak could not be obtained for the TF-LIB in this measurement. Therefore, the K-edge was determined as around 5480 eV, where the normalized absorption coefficient becomes half value (0.5). This K-edge represents the valence condition of V in the cathode layer, i.e., the K-edge energy depends on the valence of V^{21} . The K-edge energy of the reference samples (V metal, VO₂, V₂O₅) showed a clear linear relationship with the valence state of V, representing that the valance state of V in the cathode layer can be determined by the K-edge energy (Supplementary Figs. 1 and 2).



Fig. 1. Structure and charge/discharge sequence of the TF-LIB. (a) Cross-sectional view, (b) top view and (c) photograph. The thickness of the VO-LPO cathode layer is 0.25 μ m. (d) Illustration of charge/discharge sequence and conditions. Blue lines and axis represent voltage. Red lines and axis represent current.



Fig. 2. Charge/discharge characteristics of the TF-LIB from XANES. XANES spectra of (**a**) 3rd charge and (**b**) 3rd discharge. (**c**) Capacity transition and K-edge energy shift. The energy shift is based on the initial state of the K-edge energy. (The solid blue line represents the interpolation.) (**d**) Capacity transition and pre-edge peak intensity shift. (The solid red line represents the interpolation.)

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In Fig. 2a-b, the clear K-edge shift to the higher energies was observed in the charging process. This trend was also observed in the first and second charging processes, as shown in Fig. 2c. In this graph, the measured values are connected by the interpolated line, and this result represents that K-edge energy was closely linked with the charge/discharge cycles. According to the measurement of the reference samples shown in Supplementary Fig. 2, the increase in K-edge energy implies an increase in the valence of V. This is consistent with the desorption of Li ions from VO-LPO cathode upon charging. Conversely, during the discharge process, the K-edge energy decreases due to the insertion of Li ions into the cathode. The valence changes of V in the cathode were determined from the K-edge energy of the 3rd cycle. The valence of V in the fully discharged state (SOC 0% at the end of the 2nd cycle) was 4.64, and then it increased to 5.11 in the 3rd fully charged state (SOC 100%). Successively, in the 3rd fully discharged state (SOC 0%), the valence returned to the same valence number of 4.64, as shown in Supplementary Fig. 3. This indicates that the in-situ observation of the valence changes of V is possible during the charge/discharge process. However, the valence of V at full discharge, which is 4.64, is higher than the valence of 3.5 which is observed in fully lithiated crystalline $V_2 O_5^{11}$. This suggests the low Li-ion insertion into the amorphous VO-LPO cathode during discharge, i.e., low cathode active material utilization. In addition, the V valence number was estimated to be more than 5 in the fully charged state. The anomalous valence state of V is probably due to the amorphous nature of the cathode and the presence of other elements such as phosphorus.

In Fig. 2a–b, the pre-edge peak was observed at around 5468 eV. It has been reported that the pre-edge peak of vanadium oxide is associated with the dipole forbidden transition $(1s\rightarrow3d)$, which is only allowed in the case of non-octahedral symmetry²¹⁻²³. This means the intensity of the pre-edge peak depends on the coordination symmetry of V in the cathode and it increases as the octahedral symmetry of the vanadium oxide is deformed. As shown in Fig. 2a–b, the pre-edge peak intensity increases when the TF-LIB is charged and it decreases when discharged. This indicates that the symmetry around the V site decreases due to the removal of the Li ions from the cathode as the battery is charged. Conversely, when discharged, Li ions are inserted into the cathode layer and the symmetry of the V site recovers. The change in the pre-edge peak intensity is in good agreement with the SOC of the TF-LIB as shown in Fig. 2d.

EXAFS

Supplementary Fig. 5 shows the Fourier transforms of the EXAFS spectra for the reference samples (V metal, VO₂, and V₂O₅). The peak position represents the bond distance with V atom. In all reference samples, peaks were observed at bond distances longer than 1.5 Å. Previous studies reported that the V₂O₅ peak observed at 1.6 Å was due to a V-O bond in the first coordination sphere^{24–26}. Since the VO-LPO cathode layer is an amorphous phase (Supplementary Fig. 6), only the peak in the first coordination sphere (~2.0 Å) is of interest.

Figure 3a–b shows the EXAFS spectra of the 3rd charge/discharge cycle. The EXAFS data (k^2 -weighted $\chi(k)$), including the reference samples, are shown in Supplementary Fig. 4. In this measurement, clear peaks were observed at 1.2 Å, 1.7 Å, and 2.0 Å. Judging from the results of the reference samples and the previous studies, the peaks at 1.7 Å and 2.0 Å are attributed to V-O bonds^{24–26}. In particular, as shown in Fig. 3a–b, the V-O peak at about 1.7 Å in the fully discharged state was shifted to about 1.6 Å by charging. Conversely, the V-O peak returned to approximately 1.7 Å by returning to the discharged state from the charged state. Figure 3c shows a plot of the peak position of V-O bonds against the SOC. The peak position was plotted by applying cubic spline





interpolation to successive points. The shift of the peak position represents that the local structure around V changes with charge/discharge reactions. On the other hand, The V-O peak position was 1.72 Å in the initial state and 1.69 Å in the 3rd fully discharged state. Therefore, the V-O peak position does not completely return to its initial state after the charge/discharge cycle, which is probably due to the capacity degradation of the amorphous cathode.

By in-situ measurements of XANES and EXAFS, the changes of the valence, coordination symmetry, and local structure of V in the amorphous VO-LPO cathode could be observed during the charge/discharge cycle. However, the V-O bond distance in the EXAFS did not return to the initial state during the charge/discharge cycles. As shown in Fig. 3c, the full-charge capacity of TF-LIB was decreased with the charge/discharge cycles, and the same tendency was observed in the radial distance of V in EXAFS. This result suggests that the degradation of the TF-LIB capacity is closely related to the local structure of the V.

Discussion

We conducted in-situ XAFS measurements on the cathode of an all-solid-state lithium-ion thin-film battery consisting of amorphous VO-LPO/LiPON/Si films to study the electrochemical state and local structural changes of vanadium (V) during charge/discharge cycle. In the XANES measurements, the V K-edge energy shift was clearly observed due to the desorption and insertion of Li ions during charge/discharge reactions. The pre-edge peak intensity, which reflects the coordination symmetry around V, was also changed due to the desorption and insertion of Li ions into the amorphous VO-LPO cathode layer. EXAFS analysis indicated the change of the V-O bond distance in the amorphous VO-LPO cathode layer associated with the symmetry change around V. In this study, we could observe the changes in the electrochemical state and local structure of V in the amorphous VO-LPO cathode layer eaction.

Methods

Sputtering deposition of TF-LIBs

The TF-LIB was deposited by RF magnetron sputtering. We used a 20×20 mm glass substrate. First, a 0.15 µm-thick Al layer was deposited as the cathode current collector, and then, the 0.25 µm-thick VO-LPO cathode layer was deposited by co-sputtering V_2O_5 and Li_3PO_4 targets. The x-ray diffraction pattern of the VO-LPO cathode layer was shown in Supplementary Fig. 6. Except for clear Cu(111) diffraction, the broad halo diffraction was observed, indicating the VO-LPO cathode layer was an amorphous structure. Successively, a LiPON electrolyte layer (0.38 µm) was formed by sputtering Li_3PO_4 in N_2 gas. Then, a Si anode layer (0.1 µm) was deposited on the LiPON electrolyte layer and a Cu layer (0.25 µm) was deposited on the Si anode as the anode current collector. After that, a Si was deposited again on the Cu anode current collector as an encapsulation layer.

In-situ XAFS measurements

Supplementary Table 2 shows the measurement conditions of XAFS. Reference samples of V metal, VO_2 , and V_2O_5 were measured by the transmission mode. On the other hand, the TF-LIB was measured by the

fluorescence mode because of the low amount of vanadium in the TF-LIB. The measurements were repeated six times at the same measurement point to improve S/N. The sample holder was tilted slightly from the parallel axis of the incident X-ray beam path and the fluorescent X-ray from the TF-LIB was detected by a 19-element semiconductor detector (MIRION Technologies).

Data availability

The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

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Author contributions

I. K. directed and supervised the project. K. O. performed the synthesis, most of the characterizations, and performance tests. I. K, K. O. and T. W. conducted the XAFS measurements, and K. O, and S. O analyzed the experiment results. K. O. wrote the manuscript. All authors discussed the results and commented on the paper.

Declarations

Competing interests

The authors declare no competing interests.

Additional information

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Correspondence and requests for materials should be addressed to I.K.

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